SULFATE-REDUCING BIOREACTOR DESIGN AND OPERATING ISSUES: IS THIS THE PASSIVE TREATMENT TECHNOLOGY FOR YOUR MINE DRAINAGE?

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ABSTRACT

There are basically two kinds of biological passive treatment cells for treating mine drainage. ***Aerobic Cells,*** containing cattails and other plants, are typically applicable to coal mine drainage where iron and manganese and mild acidity are problematic. ***Anaerobic Cells*** or ***Sulfate- Reducing Bioreactors*** are typically applicable to metal mine drainage with high acidity and a wide range of metals. Most passive treatment systems employ one or both of these cell types. The track record of aerobic cells in treating coal mine drainage is impressive, especially in the eastern coalfields. Sulfate-reducing bioreactors have tremendous potential at metal mines and coal mines, but have not seen as wide an application.

This paper presents the advantages of sulfate-reducing bioreactors in treating mine drainage, including: the ability to work in cold, high altitude environments, handle high flow rates of mildly affected ARD in moderate acreage footprints, treat low pH acid drainage with a wide range of metals and anions including uranium, selenium, and sulfate, accept acid drainage-containing dissolved aluminum without clogging with hydroxide sludge, have life-cycle costs on the order of $0.50 per thousand gallons, and be integrated into "semi-passive" systems that might be powered by liquid organic wastes.

Sulfate reducing bioreactors might not be applicable in every abandoned mine situation. However a phased design program of laboratory, bench, and pilot scale testing has been shown to increase the likelihood of a successful design.

Additional Key Words: Constructed wetlands, acid mine drainage, heavy metals, sulfate reduction

INTRODUCTION

It has been over twenty years since the pioneering work of a group of researchers at Wright State University documented water quality improvements in a natural *Sphagnum* bog in Ohio that was receiving low pH, metal laden water (Huntsman, et al., 1978). Independently, a group at West Virginia University found similar results at the Tub Run Bog (Lang, et al., 1982). Subsequently, researchers, practitioners, and engineers focused on developing the promising technology of using "constructed wetlands" to treat acid mine drainage (AMD) or acid rock drainage (ARD). But the term "wetland," besides carrying legal and regulatory baggage, does not quite describe structures like "anoxic limestone drains" or "successive alkalinity producing systems," Hence, the term "passive treatment" was coined.

The design of passive treatment systems entails the selection of treatment "modules" appropriate to the geochemistry of the mine drainage. As shown in Figure 1, there are two geochemical "zones" in a natural wetland ecosystem. The lower, oxygen-depleted, zone is where sulfate-reducing bacteria thrive. The focus of this paper is the design of passive treatment modules that capitalize on the geochemical reactions typically found in the anaerobic zone of natural systems.

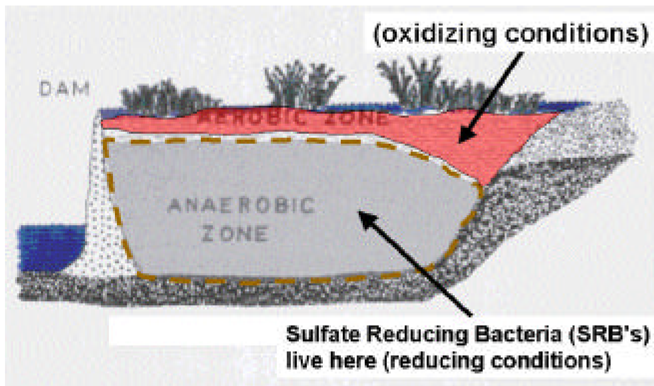


Figure 1. Typical Natural Wetland Geochemical Zones

Definition of Passive Treatment

There are many technologies for treating AMD/ARD. To properly focus the discussion, the following definition of passive treatment is proposed:

> ***Passive treatment*** is a process of sequentially removing metals and/or acidity in a natural-looking, man-made bio-system that capitalizes on ecological and geochemical reactions. The process requires no power and no chemicals after construction and lasts for decades with minimal human help.

It is a ***sequential*** process because no single treatment cell type works in every situation or with every AMD/ARD geochemistry. It is an ***ecological/geochemical*** process because most of the reactions (with the exception of limestone dissolution) that occur in passive treatment systems are biologically assisted. Finally, it is a ***removal*** process because the system must involve the filtration or immobilization of the metal precipitates that are formed.

A truly passive system should also function for many years, without a major retrofit to replenish construction materials, and without the use of electrical power. Benning and Ott (1997) described a volunteer passive system outside of an abandoned lead-zinc mine in Ireland that has been functioning unattended for over 120 years. Ideally, a passive treatment system should be designed to last for at least several decades without reconstruction.

METAL REMOVAL AND OTHER BIO-GEOCHEMICAL MECHANISMS IN PASSIVE TREATMENT SYSTEMS

Many physical, chemical, and biological mechanisms occur within passive treatment systems reducing the metal concentrations and neutralizing the acidity of the incoming flow streams. Notable mechanisms include:

- Sulfide and carbonate precipitation catalyzed by sulfate-reducing bacteria (SRB) in anaerobic zones
- Hydroxide and oxide precipitation catalyzed by bacteria in aerobic zones
- Filtering of suspended material
- Metal uptake into live roots and leaves
- Adsorption and exchange with plant, soil, and other biological materials.

Wildeman, et al. has determined that plant uptake does not contribute significantly to water quality improvements in passive treatment systems (1993). However, plants replenish systems with organic material and add aesthetic appeal. In aerobic systems, plant-assisted reactions appear to aid overall metal removal performance, perhaps by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis-related reactions and respiration in the plant root zone. Plants also appear to provide attachment sites for oxidizing bacteria/algae. Research has shown that microbial processes are a dominant removal mechanism in passive treatment systems (Wildeman, et al., 1993).

Sulfate Reducing Bioreactors

Sulfate reduction has been shown to effectively treat AMD/ARD containing dissolved heavy metals, including aluminum, in a variety of situations. The chemical reactions are facilitated by the bacteria ***desulfovibrio*** in sulfate-reducing bioreactors as shown in Figure 2 in schematic form and the photo in Figure 3.

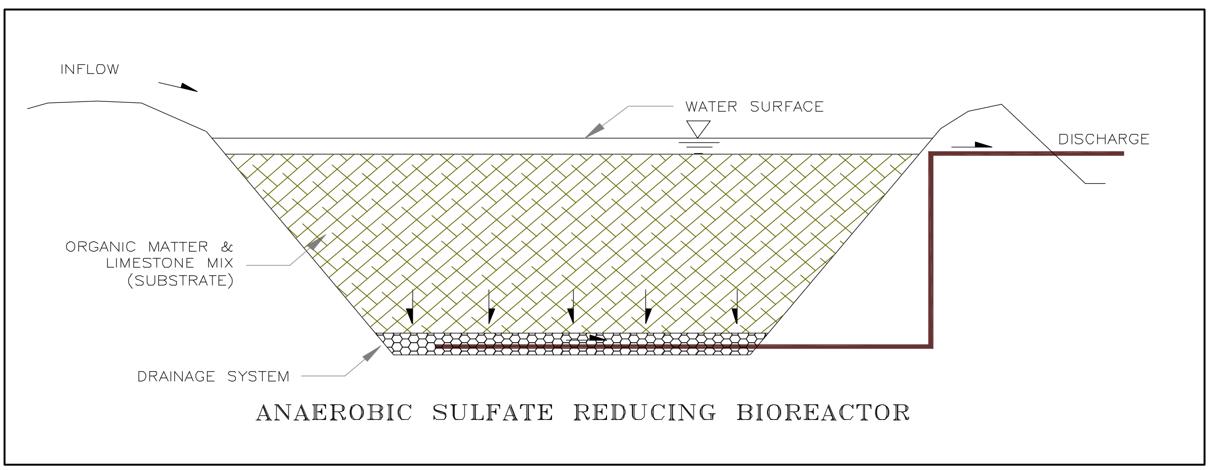


Figure 2. Sulfate-Reducing Bioreactor Schematic

Figure 3. A Typical Sulfate-Reducing Bioreactor

The sulfate-reducing bacterial reactions (equation 1) involve the generation of:

- Sulfide ion (S^{-2}), which combines with dissolved metals to precipitate sulfides (equation 2)
- Bicarbonate (HCO_3^-), which has been shown to raise the pH of the effluent

The sulfate reducing bacteria produce sulfide ion and bicarbonate as shown in the following reaction (Wildeman, et al., 1993):

1) $$SO_4^{-2} + 2\ CH_2O\ ?\ \ S^{-2} + 2\ HCO_3^{\ -} + 2\ H^+$$

The dissolved sulfide ion precipitates metals as sulfides, essentially reversing the reactions that produce AMD/ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):

2) $$Zn^{+2} + S^{-2}\ ?\ \ ZnS$$

Suspected geochemical behavior of aluminum in sulfate reducing bioreactors has been documented (Thomas and Romanek, 2002). It is suspected that insoluble aluminum sulfate forms in the reducing environments found in sulfate-reducing bioreactors, perhaps in accordance with the following reaction which is one of many possible:

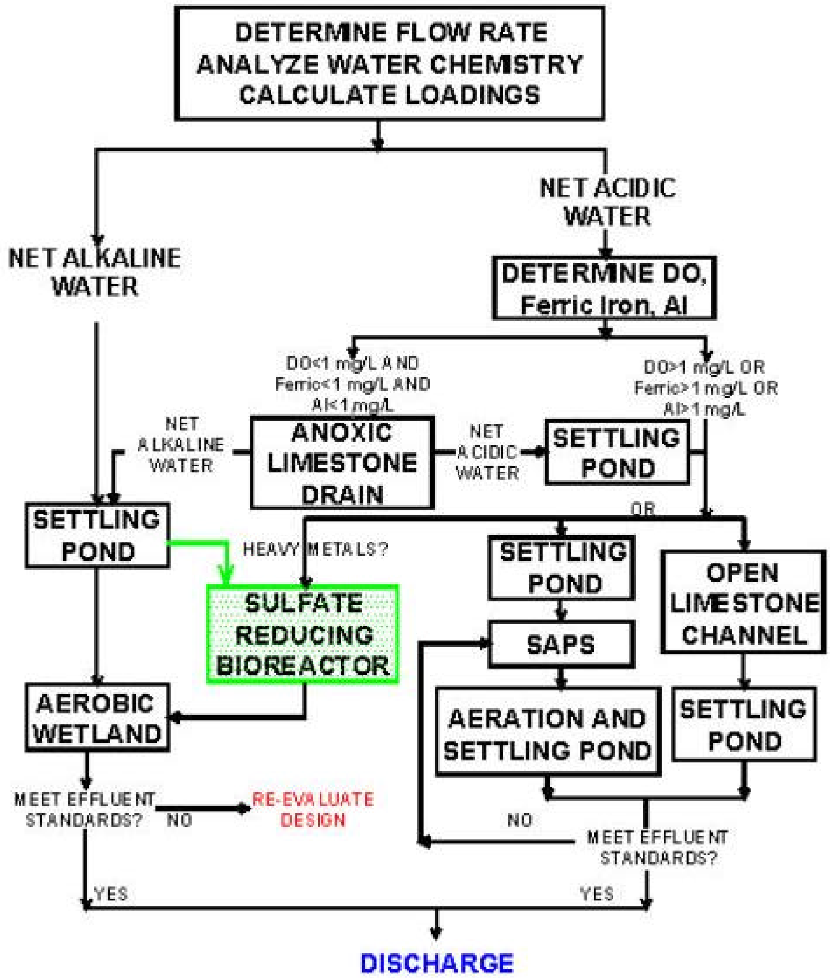
3) $$3Al^{3+} + K^+ + 6H_2O + 2SO_4^{2-}\ ?\ \ KAl_3(OH)_6(SO_4)_2\ (Alunite) + 6H^+$$

The key conditions for SRB health are a pH of 5.0 (maintained by the SRB itself through the bicarbonate reaction and/or the presence of limestone sand), the presence of a source of sulfate (typically from the AMD/ARD), and organic matter ([CH_2O] from the substrate). Sulfate-reducing bioreactors have been successful at substantially reducing metal concentrations and favorably adjusting pH of metal mine drainages.

FLOW CHART FOR PASSIVE TREATMENT SYSTEM DESIGN

In the late 1980s, the design methods for aerobic passive treatment cells for iron removal were still under development. Brodie (1991) sorted out the empirical relationships in a milestone design flow chart that provided the foundation for a more comprehensive design flow chart subsequently developed by Hedin and Nairn at the former U.S. Bureau of Mines as shown in Figure 4.

This figure, in one form or another, continues to guide engineers and practitioners in the passive treatment cell design process. It has been modified by the author to include the passive treatment of heavy metal-bearing AMD/ARD based on observations since 1988. The sulfate-reducing bioreactor as shown reflects where this particular technology fits in the design philosophy. Although the technology is well suited for AMD/ARD with net acidity and/or heavy metals, it can also be effectively applied to net alkaline water sources as indicated by the arrow drawn from the settling pond on the left hand side of the flow chart



.Figure 4. Flow Chart for Selecting a Passive AMD Treatment System Based on Water Chemistry and Flow (Adapted from Hedin, et al., 1994).

PHASED DESIGN PROTOCOL

There is no “cookbook” design manual for passive treatment systems although the design flow chart above is a safe starting point. A phased approach design project is recommended; it typically begins in the laboratory with static tests, graduating to final testing phases (bench and pilot) performed at the site on the actual AMD/ARD. Bench scale testing will determine if the treatment technology is a viable solution for the AMD/ARD and will narrow initial design variables for the field pilot. A proper bench scale test will certainly reduce the duration of the more costly field pilot test. Field pilot test duration can range from days, to months, to years, depending on the nature of the technology. Depending on the nature of the equipment and personnel needed, significant costs may be incurred during the field pilot tests – about $500 to $1,000 per week, mostly for sampling and analysis. Compare this to $5,000-$10,000 per week for active treatment pilot tests. More detailed descriptions of laboratory, bench, and pilot tests are provided in Gusek (2001).

ADVANTAGES OF SULFATE-REDUCING BIOREACTORS

As shown in Figure 4, sulfate-reducing bioreactors can be applied in a number of different AMD/ARD situations. While most passive treatment systems (both aerobic zone and anaerobic zone types) offer simplicity of design and operation and economic advantages over active/chemical treatment, sulfate-reducing bioreactors have advantages worth considering.

- No aluminum plugging
- Can easily handle low flow net acidic water or high flow net alkaline water
- Uses waste organic materials
- Resilient to loading and climate variations
- Consumes sulfate; capable of treating selenium and uranium
- Generates more net alkalinity in effluent
- Burial to minimize vandalism
- Opportunities for community involvement in organic procurement
- Might be able to construct them in abandoned underground mines

Brief discussions of these issues follow.

No Aluminum Plugging

When AMD/ARD attacks clay-bearing formations at mining sites, significant amounts of dissolved aluminum can be created. The geochemistry of aluminum is complex, and this can cause problems in passive treatment systems. The formation of the mineral gibbsite [Al $(OH)_3$] is especially problematic as it is a gelatinous solid. Gibbsite tends to form in limestone-dominated passive treatment cells, and the sludge tends to plug the void spaces between the limestone rock, becoming a major maintenance problem. While the precise mechanisms are just beginning to be understood (Thomas and Romanek, 2002), the precipitation of gibbsite is avoided in SRB cells. It is suspected that unidentified alternative aluminum compounds form in the SRB cells instead of gibbsite, and these compounds are less prone to plugging. Several case histories of SRB passive treatment projects that involved treating ARD with high aluminum concentrations are provided in Gusek and Wildeman (2002)

Use of Waste Materials in Construction

Organic materials are a key component in the formulation of the substrate of sulfate-reducing bioreactors. Often these materials are considered waste materials and can be obtained for little or no purchase cost. The only expense incurred might be in their transport to the treatment site. If the site is in a remote forest environment, some of the materials such as wood chips and sawdust might be generated onsite or from local sources. A short list of organic waste materials, both solid and liquid, that might be candidates for use in a sulfate-reducing bioreactor is provided below. The list is not necessarily all inclusive as specialty wastes unique to different locales might be available.

- Wood chips
- Sawdust
- Hay and straw (spoiled)
- Cardboard?

- Yard waste
- Mushroom compost
- Animal manure
- Partially treated sewage?
- Waste alcohols including antifreeze
- Waste dairy products
- Sugar cane processing residue (Bagasse)

Using liquid organic wastes poses a specific opportunity and challenge. These materials are typically very biodegradable and as such are considered "candy" to sulfate-reducing bacteria. Thus, they are consumed quickly and need to be replenished on a nearly continual basis. This is not consistent with the strict definition of passive treatment cited earlier. However, since these materials might be stored in tanks or fed continuously from offsite sources through pipelines, systems using these waste organic sources would be considered "semi-passive" in nature. Such cells are often called "enhanced sulfate-reducing bioreactors" due to the boost provided by the liquid organic material. When alcohol is the chosen enhancer, the technique has sometimes been called "bugs on booze."

<u>Resilient to Loading and Climate Variations</u>

If properly designed, sulfate-reducing bioreactors can be resilient to metal-loading variations. Pilot scale tests are the best venue for establishing the expected operating ranges of flow and metal concentrations and the reactions of the SRB cells to those varying conditions. For example, a pilot SRB cell at a lead mine in Missouri was sized for 25 gpm. Once steady state operation was observed for many months, the flow was increased to nearly double the design rate. The SRB cell began to show evidence of stress (i.e., decreased metal removal efficiency) after several months of exposure to the higher flow (Gusek, et al., 1998). Not all SRB cells might be this resilient, but this observation allowed engineers to include a significant factor of safety in the design of the full-scale system (1,200 gpm capacity) at this site.

Low temperature operation is a major concern at some sites, especially in the mountainous states in the west and Appalachia. Pilot cell data at the Ferris Haggarty Copper Mine/Osceola Tunnel Site in Wyoming at elevation 9,500 feet suggests that sulfate reduction rates decline in cold weather, but the decrease is not significant enough to render the design concept untenable. At this site, the typical water temperature is about 4ºC. Winter operational data revealed that the cell continued to function at temperatures less than 1ºC, and the sulfate reduction rate was estimated to be about 0.24 moles per day per cubic meter ($m/d/m^3$) (Gusek, 2000). Compared to the benchmark design value of 0.3 $m/d/m^3$, this constitutes a 20 percent decrease.

<u>Sulfate-Reducing Bioreactors Consume Sulfate; Selenium and Uranium Reduced</u>

Sulfate is a component of AMD/ARD that may be receiving more regulatory attention. It contributes to the total dissolved solids (TDS) concentration. But unlike other TDS constituents such as sodium, chlorine, and calcium, it is not conservative and can be mitigated in sulfate-reducing bioreactors. No other passive treatment technique has this capability as its primary function. Some sulfate reduction is typically observed in Successive Alkalinity Producing Systems (SAPS) (see Kepler and McCleary, 1994), but their primary function is to add alkalinity through limestone dissolution.

While sulfate-reducing bioreactors are naturally efficient at consuming sulfate, the geochemical conditions generated in a typical cell are also conducive to reducing selenium from the dissolved state to elemental selenium; this is facilitated by selenium-reducing bacteria. They are also effective in reducing uranium from the oxidized state to form insoluble uranium oxide similar to the way that some natural uranium deposits formed.

Burial to Minimize Vandalism

Any passive treatment system might be a target for vandalism. Because neither plants nor air are required for the sulfate-reducing bioreactors to function, they can be buried beneath a veneer of rock and soil provided that the feed water plumbing to the cell is not compromised. Settlement of the organic substrate needs to be considered in the design if burial is being considered. However, most organic substrate designs typically include a large component of wood chips or sawdust, which do not readily compress under minor surcharge loads developed by soil/rock covers. This aspect of the design should ideally be evaluated at the pilot stage of the design effort.

Underground In-Mine Treatment Systems

As stated above, one of the beauties of SRB systems is that they do not require plants to operate. All that is needed is a carbon source and an SRB arranged in a manner that encourages bacterial growth in concert with managed loading of AMD/ARD. In areas where land surface favorable to passive treatment system construction is at a premium due to steep terrain or the encroachment of civilization, building passive treatment systems in abandoned underground mine voids (using the mine void itself as the containment "vessel") is an attractive possibility that has been realized in only one study at a metal mine in Montana (Canty, 1999).

Two challenges to overcome to implement this technology include the placement of large volumes of solid organic matter into mine voids through boreholes and the procurement of inexpensive organic material like forestry or paper waste and animal manure (SRB inoculum). The introduction of animal manure (even in small amounts) into ground water (i.e., a mine pool) will be a regulatory hurdle that may prove to be difficult to surmount. Carefully controlled field tests in small mines will probably be required.

Low Flow Net Acidic Water or High Flow Net Alkaline Water

At a given flow rate, the footprint of a sulfate-reducing bioreactor is governed by the mineral acidity of the AMD/ARD. The higher the acidity, the larger the surface area is required per unit of flow. The land area available for the system may be limited, especially for high flows of net alkaline AMD/ARD. In this situation, the surface area of the SRB cell might be as small as 10 square feet per gpm of flow. Thus, a net alkaline flow of 2,000 gpm might require as little as 20,000 square feet or about half an acre of cell. Cell depth will be a function of metal load.

Conversely, a very acidic AMD/ARD source might require a similar area to treat a significantly less rate of flow. For example, a flow of only 30 gpm of AMD with over 2,000 mg/L of acidity would require nearly 3 acres of surface area. However, there are no other technologies capable of passively treating AMD/ARD with this aggressive a chemistry.

Added Net Alkalinity in Effluent

Sulfate-reducing bioreactors are typically sized to deliver treated water with low concentrations of metals and a near neutral pH. However, experience has shown that SRB cell effluents typically contain excess alkalinity at concentrations above those expected from SAPS units or anoxic limestone drains. This excess alkalinity is therefore available to ameliorate acidity contributions that might be impacting the receiving stream far removed from the original passive treatment site.

New Opportunities for Community Involvement

The construction of passive treatment systems is an ideal way to make the most of community volunteerism. The transplanting of wetland vegetation is the most common activity in which volunteers can become involved with passive treatment projects. However, the collecting of organic materials for sulfate-reducing bioreactor substrate opens an entirely new opportunity for local community organizations to release pent-up volunteerism. Some pet owners are often hard pressed to find useful and environmentally sound ways to dispose of significant amounts of manure (e.g., horse). Homeowners could divert tree trimmings or yard waste away from the local landfill and into a community stockpile of wood waste to be mulched (but not composted) and used in a nearby sulfate-reducing bioreactor. Farmers would have a place to dispose of moldy hay. Community events similar to paper drives could be used to collect materials in advance of a project. This not only lowers the cost of the project but also provides additional community buy-in.

SULFATE-REDUCING BIOREACTOR DESIGN EXAMPLES

Design Example No. 1

This is a hypothetical abandoned underground coal mine in Appalachia with a relatively small mine pool. The site is adjacent to a fresh water lake. The flow varies through the year, but the AMD chemistry is fairly constant. SAPS had been considered at this site but rejected due to the elevated aluminum concentration. Pertinent design parameters are listed below.

- 67 gpm peak flow
- pH = 2.5
- Fe = 152 mg/L (ferric iron)
- Aluminum = 30 mg/L
- Acidity = 500 mg/L
- 990 moles of Fe per day

The hypothetical passive treatment system will include two sulfate-reducing bioreactors (each treating 50 percent of the flow) to raise the pH, produce net alkalinity and remove nearly 100 percent of the aluminum and 95 percent of the iron. The system would be comprised of the following components:

- 1.7 acres of SRB cell 3 feet deep

- 0.25 acres of aerobic polishing cell

The costs of developing this design from initial concept to complete construction include:

- $30,000 to $50,000 for bench and pilot studies
- $315,00 design and construction (assuming no donated materials or labor)

The 8,250 cubic yards of organic substrate originally installed would require replacement every 20 to 30 years. The substrate typically comprises about 33 percent of the construction cost. This would be about $110,000 or less depending on the availability of local materials and in-kind donations. This and other maintenance costs are summarized on an annual basis in the table below. Some of these costs might be minimized through volunteer labor and other contributions.

Maintenance Item	**Annual Cost**
Replace Substrate	$3,569
Dispose Substrate (20% of replacement cost.)	$714
Weekly inspection & pipe clean?	$5,000
Flushing for aluminum buildup	$0
Sampling/lab costs lump sum	$15,000
	$24,283

The life cycle cost of this treatment (includes capital and operating cost) is about $0.70 per thousand gallons treated.

Design Example No. 2

This is another hypothetical abandoned underground coal mine in Appalachia but with a relatively large mine pool covering over 100,000 acres. The site contributes nearly 50 percent of the metal load to a nearby river. The flow is relatively steady through the year, and the AMD chemistry is constant as well. The site has only 6 acres available for construction of a main treatment system, but there are no restrictions on effluent polishing. This is a major project due to the flow rate. Pertinent system design parameters are listed below.

- 3,000 gpm from a deep mine pool
- Sulfate = 1000 mg/L (50 effluent goal)
- pH = 5.5
- Fe^{+2} = 150 mg/L
- Al =2 mg/l
- Mn = 2.7 mg/L (0.05 effluent goal)
- Acidity = 50 mg/L (“Hot Acidity”)

The 6-acre restriction eliminates a standard sulfate-reducing bioreactor. However, an enhanced sulfate-reducing bioreactor (ESRB) is feasible due to the steady availability of a waste alcohol product and other factors. The enhancement allows the footprint of the ESRB cell to shrink and easily fit in the space available. The ESRB effluent will have a neutral pH and some excess alkalinity. However, it will also have elevated biological oxygen demand (BOD) and manganese, which require further polishing. Key features of this hypothetical system include:

- 4 acres of enhanced sulfate-reducing bioreactor cell 6 feet deep
- 9 acres of aerobic polishing cell (for Mn and BOD treatment)

The costs of developing this design from initial concept to complete construction include:

- $200,000 for bench and pilot studies
- $1.36M design and construction

The operating cost of the enhanced sulfate-reducing bioreactor (including paying $2.00 per gallon for the alcohol) is $674,000 per year or $0.43 per 1000 gallon treated. The system effluent would meet drinking water standards. To be conservative, the above cost assumes that the substrate in the ESRB be replaced every 20 to 30 years due to metal sulfide precipitate buildup.

<u>Design Example No. 3 - Do SRBs Need More Room?</u>

This design example compares the area requirements for using a standard aerobic wetland and a standard sulfate-reducing bioreactor to treat a relatively large net alkaline flow. The design assumptions are listed below.

- 3,000 gpm from a deep mine pool
- pH = 6.5
- Fe+2 = 50 mg/L (817,560 grams/day or 14,638 moles per day)
- Net alkaline
- No manganese
- 10 acres available for main treatment cells

If an aerobic wetland dominated by cattails and other vegetation was designed on the standard assumption of 11 grams/day per square meter of iron loading criteria (which was established by U.S. Bureau of Mines researchers), approximately 18 acres of wetland habitat would be needed.

A sulfate-reducing bioreactor with an identical treatment capacity would cover 8 acres (probably split into four 2-acre cells plumbed in parallel). The cells would be 7.5 feet deep, and the AMD/ARD would enter them at the bottom and exit at the top. This upflow configuration allows the top of the cell to function as a primary dissolved oxygen polishing cell. The remaining available 2 acres would be fitted with a final aerobic polishing cell to complete the facility. In this situation, both cell types would work geochemically, but only one – the sulfate-reducing bioreactor – would be feasible.

SUMMARY

Sulfate-reducing bioreactors are not the only type of passive treatment technique available to the design engineer, and they are not applicable in every situation. However, they can handle a wide variety of flows and AMD/ARD chemistries in hostile cold climates, and they can treat aluminum-bearing AMD/ARD without plugging. Furthermore, they can generate excess alkalinity in their effluent that further enhances the quality of the receiving stream.

Sulfate-reducing bioreactors typically require large amounts of organic materials that are usually considered waste. Enhanced SRB cells can consume liquid organic wastes like antifreeze or cheese whey.

While not readily practiced, it may be feasible to build them in mine voids to provide in situ treatment at sites with limited land area.

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